

# Chromate Diffusion and Reduction in Soil Aggregates: Dynamics of Contamination and In-situ Reduction

*T.K. Tokunaga<sup>1</sup>, J. Wan<sup>1</sup>, T.C. Hazen<sup>1</sup>, M.K. Firestone<sup>2</sup>, E. Schwartz<sup>2</sup>, K.R. Olson<sup>1</sup>, S.R. Sutton<sup>3</sup>, A. Lanzirotti<sup>3</sup>, W. Rao<sup>4</sup>*

<sup>1</sup> Lawrence Berkeley National Laboratory

<sup>2</sup> University of California, Berkeley

<sup>3</sup> University of Chicago

<sup>4</sup> University of Georgia

The fate of metal contaminants in soils and sediments is controlled by interdependent influences of biogeochemical reactions and transport. In order to characterize individual reactions, they are typically investigated in well-mixed batch systems of fairly simple composition. However, subsurface chemical transport often occurs via a multitude of microenvironments, each having their own distinct chemical and microbial characteristics. The gap between the understanding of simple batch systems and observations on complex natural subsurface systems motivates the examination of biogeochemical dynamics in systems of intermediate complexity. Such a manageable level of complexity is found within individual soil aggregates and sediment blocks. Soil aggregates (cohesive units comprised of individual mineral particles) and sediment blocks can contain wide variations in chemical and microbiological composition, especially when intra-aggregate gradients in redox potentials exist. We have examined influences of aggregate microenvironments and microbial communities that control the fate of Cr(VI) contamination. Under typical subsurface conditions the two dominant Cr oxidation states have widely different behavior [1]. The Cr(VI) species are generally more soluble and mobile, as well as more toxic. More reducing conditions favor stability of less soluble, strongly sorbing, less mobile, and much less toxic Cr(III) species. Hence, it is essential to distinguish between these two oxidation states in the environment.

Two components of our research are summarized in this article. The first is on the Cr(VI) contamination process, examining the influence of microbial activity on the fate of Cr(VI) diffusing into soil aggregates. The second part of our study tests the effectiveness of adding organic carbon for accelerating in-situ Cr(VI) reduction in sediments. Both parts of this study rely on the x-ray microprobe and micro-XANES for mapping total Cr, Cr(VI) and Cr(III) concentrations in soils. Beamline X26A at NSLS, and the GeoSoilEnviroCARS beamline 13ID-C were used to obtain these element and oxidation state maps. The normalized pre-edge

peak intensity of the Cr K-edge was used to determine the fraction of total Cr occurring as Cr(VI) [2].

Our Cr contamination experiments were conducted on soil aggregates that were previously incubated with varying levels of organic carbon in order to establish a range of initial levels of microbial activity, then exposed to Cr(VI) solutions. The Cr(VI), applied at concentrations as high as 5,200 ppm, was allowed to diffuse into the aggregates and become reduced to Cr(III) wherever local conditions favored this reaction. In general, soils with higher organic matter content and higher microbial activity had higher levels of Cr(VI) uptake, higher proportions of Cr(VI) reduced to Cr(III), and shorter transport distances. Thus, reduction of Cr(VI) to Cr(III) occurred only within the surface layer of aggregates with higher available organic carbon and higher microbial respiration. Sharply terminated Cr diffusion fronts develop when the reduction rate increases rapidly with depth. The final state of such aggregates consists of a Cr-contaminated exterior, and an uncontaminated core, each having different microbial community compositions and activity. These trends were first identified in studies on synthetic soil aggregates [3], and were more recently observed in experiments on intact, natural soil aggregates (Figure 1). The x-ray microprobe maps of Cr distributions in these contaminated field soil aggregates exhibited radial concentration patterns that were very consistent with the earlier results on synthetic aggregates.

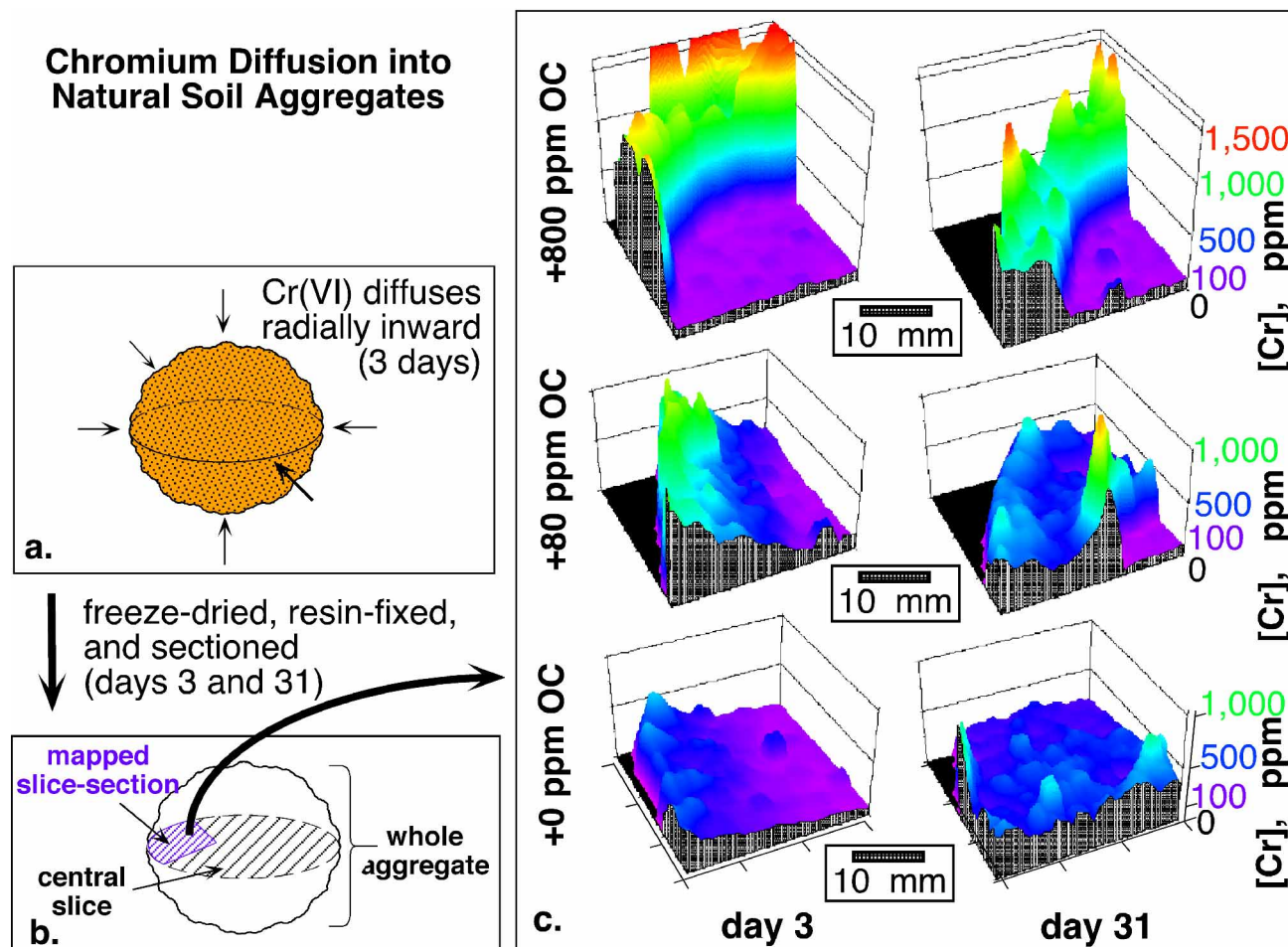
A number of pathways contribute to the overall observed Cr(VI) reduction rates and spatial distributions of Cr. In these neutral to slightly alkaline soils, Cr(VI) reduction by Fe(II) becomes very important as the redox potential decreases. Aqueous Fe(II) concentrations increase as redox potentials are lowered as a result of microbial respiration and diffusion-limited resupply of oxygen. Some microorganisms are also capable of direct, enzymatic Cr(VI) reduction [4]. Comparisons between Cr(VI) reduction rates due to direct microbial versus Fe(II) pathways indicate that the latter is probably dominant in reducing sediments. Nev-

ertheless, microorganisms exert the dominant influence in reducing sediments since their respiration is responsible for the availability of Fe(II).

Analogous behavior may be expected for other redox-sensitive transformations in soils and sediments. Locally high microbial activity and reaction rates that are limited by transport are basic requirements for the reductive deposition of metal contaminants. These results also show that commonly employed geochemical and microbiological measurements on soils that average over larger volumes cannot detect important finer scale, transport-limited features.

The second phase of our study started with rapid Cr(VI) contamination of soil columns having low initial microbial activity. Later addition of organic carbon, simulating a remediation action, enhanced Cr(VI) reduction. However, much lower Cr reduction rates were achieved in these experiments. Reduction rates in the remediation tests were typically about 4 orders of magnitude lower than the rates obtained in the more reduc-

ing aggregates. The other major differences observed in the remediation experiments were lower microbial activity, higher redox potentials, and relatively uniformly distributed Cr species within soil columns throughout the experiment, showing no zonation. The very different reduction rates and spatial distributions of Cr species in these two studies can be understood through analysis of initial conditions, transport rates and reduction kinetics. In these remediation tests, the rapid injection of Cr(VI) into oxidizing soils prevented significant short term reduction to Cr(III). The chemically oxidizing and toxic effects of highly concentrated Cr(VI) solutions (up to 10,000 ppm) immediately depleted the low initial inventory of reductants, and also strongly depressed microbial activity. Thus, neither the Fe(II) nor enzymatic pathways could function at high rates. Nevertheless, reduction did occur, and followed effective 1<sup>st</sup>-order kinetics with respect to Cr(VI) and with respect to the initial amount of available organic carbon.



**Figure 1.** Natural soil aggregate contamination with Cr(VI). (a) Radial diffusion of Cr(VI) into soil aggregates (pre-incubated with different levels of organic carbon). (b) Samples preserved by freeze-drying, resin-fixing, and slicing for x-ray mapping. (c) Total Cr distributions within sections of aggregates at day 3 and day 31 relative to initial contamination event.

## Acknowledgments

We thank Robert Giauque, Tracy Letain, Dominique Joyner, and Andrew Mei of LBNL, and GSECARS staff for assistance. Funding was provided through the U. S. Department of Energy, Natural and Accelerated Bioremediation Research Program, and Basic Energy Sciences, Geosciences Program, under contract No. DE-AC03-76SF00098. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. Research carried out (in part) at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U. S. Dept. of Energy, Division of Materials Sciences and Division of Chemical Sciences, under Contract No. DE-AC02-98CH10886.

## References

- [1] D. Rai, L.E. Eary, J.M. Zachara, "Environmental Chemistry of Chromium", Science of the Total Environment, 86, 15-23, 1989.
- [2] S. Bajt, S.B. Clark, S.R. Sutton, M.L. Rivers, J.V. Smith, "Synchrotron X-ray Microprobe Determination of Chromate Content Using X-ray Absorption Near-Edge Structure", Analytical Chemistry, 65, 1800-1804, 1993.
- [3] T.K. Tokunaga, J. Wan, M.K. Firestone, T.C. Hazen, E. Schwartz, S.R. Sutton, M. Newville, "Chromium Diffusion and Reduction in Soil Aggregates", Environmental Science and Technology, 35, 3169-3174, 2001.
- [4] D.R. Lovley, "Dissimilatory Metal Reduction", Annual Reviews in Microbiology, 47, 263-290, 1993.
- [5] S. Fendorf, B.W. Wielinga, C.M. Hansel, "Chromium Transformations in Natural Environments: The Role of Biological and Abiological Processes in Chromium(VI) Reduction", International Geology Review, 42, 691-701, 2000.